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ON THE ANOMALOUS DISPERSION AND ABSORPTION OF ELECTRIC WAVES. PART V. ANOMALOUS DISPERSION AND DEBYE'S DIPOLE THEORY (CONTINUED).[1]

By San-ichiro MIZUSHIMA.

Received June 14, 1926. Published August 28, 1926.

Electric waves of the wave lengths of 3.08 metres and 50 metres were generated. Measurements of dielectric constants and absorptions were carried out according to the method described in Part II of the present report[2]. The experimental results were interpolated and the values at every ten degrees of temperature are shown in the following tables.

$\varepsilon_{obs.}$: Dielectric constant,
ε_0 : Static dielectric constant,
ε_∞ : Square of the index of refraction for visible light (D line),
K : Electric conductivity which is equivalent to anomalous absorption ($cm.^{-1}$ ohm^{-1}),
η : Viscosity.

TABLE 1.

Ethyl alcohol

$a = 1.8 \times 10^{-8}$ cm.

Temp.	η	ε_0	$\lambda = 50$ m.			$\lambda = 3.08$ m.			ε_∞
			$\varepsilon_{calc.}$	$\varepsilon_{obs.}$	$K \times 10^5$	$\varepsilon_{calc.}$	$\varepsilon_{obs.}$	$K \times 10^5$	
60°	—	—	—	—	—	—	20	3	—
50	—	—	—	—	—	—	21	4	—
40	—	—	—	—	—	—	22.5	5	—
30	—	—	—	23.5	< 1.0	—	23.5	8	—
20	0.0119	25.8	26	25	〃	25	25	13	1.85
10	0.0145	27.0	27	26.5	〃	26	26.5	21	1.86
0	0.0177	28.4	28	28	〃	26.5	28	32	1.88
−10	0.0218	30.3	30	29.5	〃	26.5	28	49	1.90
−20	0.0276	32.0	32	31.5	〃	25.5	26	72	1.91
−30	0.0358	33.7	34	33	〃	23	21.5	80	1.92
−40	0.0490	35.3	35	35	〃	18	17.5	80	1.94
−50	0.0684	37.6	37	37	〃	13	13.5	67	1.96
−60	0.0959	39.7	39	39	1.2	9	9	47	1.98

(1) Details of these papers will appear in near future in the *Journal of the Faculty of Science, Imperial University of Tokyo.*
(2) Mizushima, this journal, 1 (1926), 83.

TABLE 2.

Propyl alcohol

$a = 2.0 \times 10^{-8}$ cm.

Temp.	η	ε_0	$\lambda = 50$ m.			$\lambda = 3.08$ m.			ε_∞
			$\varepsilon_{calc.}$	$\varepsilon_{obs.}$	$K \times 10^5$	$\varepsilon_{calc.}$	$\varepsilon_{obs.}$	$K \times 10^5$	
60°	—	—	—	—	—	—	17	3	—
50	—	—	—	17	< 1.0	—	18	5	—
40	—	—	—	18.5	〃	—	19	8	—
30	—	—	—	20	〃	—	20	12	—
20	0.0226	22.2	22	21.5	〃	20	20.5	21	1.92
10	0.0292	23.5	23	23	〃	19	20	34	1.94
0	0.0388	24.8	25	24	〃	17	17.5	48	1.95
−10	0.0513	26.2	26	25.5	〃	14	14	58	1.97
−20	0.0716	27.5	27.5	27.5	〃	10.5	11	50	1.98
−30	0.103	29.0	28.5	29	〃	7	8	34	2.00
−40	0.154	30.5	29	30	1.2	5	6.5	22	2.02
−50	0.236	32.0	27.5	29	2.7	3.5	5.5	14	2.03
−60	0.386	33.7	22.5	24	4.8	3	5	9	2.05

TABLE 3.

Isobutyl alcohol

$a = 2.0 \times 10^{-8}$ cm.

Temp.	η	ε_0	$\lambda = 50$ m.			$\lambda = 3.08$ m.			ε_∞
			$\varepsilon_{calc.}$	$\varepsilon_{obs.}$	$K \times 10^5$	$\varepsilon_{calc.}$	$\varepsilon_{obs.}$	$K \times 10^5$	
60°	—	—	—	—	—	—	14	3	—
50	—	—	—	16	< 1.0	—	15	6	—
40	—	—	—	17	〃	—	16	10	—
30	—	—	—	18.5	〃	—	16.5	18	—
20	0.0391	20.0	20	19.5	〃	15.5	16	29	1.95
10	0.0555	21.0	21	21	〃	13	13	39	1.97
0	0.0804	21.8	22	22	〃	10	10	42	1.99
−10	0.116	23.2	23	23.5	〃	7	6.5	35	2.00
−20	0.182	24.5	23.5	24	1.3	4.5	4.5	17	2.02
−30	0.30	25.7	22.5	23.5	2.6	3	4	7	2.03
−40	0.56	27.0	17.5	18.5	4.1	2.5	3.5	4	2.05
−50	1.14	29.0	10	10	4.0	2	3	3	2.07
−60	—	—	—	6	2.6	—	3	2	—

TABLE 4.

Amyl alcohol

$\alpha = 2.1 \times 10^{-8}$ cm.

Temp.	η	ε_0	$\lambda = 50$ m.			$\lambda = 3.08$ m.			ε_∞
			$\varepsilon_{calc.}$	$\varepsilon_{obs.}$	$K \times 10^5$	$\varepsilon_{calc.}$	$\varepsilon_{obs.}$	$K \times 10^5$	
60°	—	—	—	—	—	—	12	3	—
50	—	—	—	—	—	—	13	5	—
40	—	—	—	—	—	—	13.5	9	—
30	—	—	—	—	—	—	13.5	17	—
20	0.0437	16.0	16	15	< 1.0	13	13	26	1.98
10	0.061	16.8	17	16.5	〃	10.5	10.5	33	2.00
0	0.0876	17.5	17.5	17.5	〃	7.5	7.5	30	2.02
−10	0.130	18.6	18.5	18.5	〃	5.5	5.5	20	2.03
−20	0.207	19.7	18.5	19	1.0	4	4	10	2.05
−30	0.33	20.8	18	17.5	2.2	3	3.5	4	2.07
−40	0.58	21.8	14	13	3.6	2.5	3	3	2.08
−50	1.01	23.0	9	8	3.0	2	3	2	2.10
−60	—	—	—	5.5	1.7	—	3	2	—

TABLE 5.

Glycerine

Temp.	ε $\lambda = 1000$ m. (Graffunder)	$\lambda = 50$ m.		$\lambda = 3.08$ m.		ε $\lambda = 1.36$ m. (Bock)
		$\varepsilon_{obs.}$	$K \times 10^5$	$\varepsilon_{obs.}$	$K \times 10^5$	
60°	36	—	—	—	—	35
50	38	37	< 1.0	40	36	36
40	39	39	〃	40.5	58	33
30	41	40.5	〃	38	90	25
20	43	43	〃	28.5	95	14
10	45	44	2.0	14	55	5
0	47	36	4.0	9	30	3.5
−10	—	23	5.6	7	14	3
−20	—	13	2.4	5	6	3
−30	—	8	< 1.0	4.5	3	3
−40	—	6	〃	4	< 2	3
−50	—	5	〃	3.5	〃	3
−60	—	4.5	〃	3	〃	3

The variation of dielectric constants and absorptions due to temperature observed at a constant wave length is, in general, quite analogous to that for the wave of 9.5 metres (see Part II and III).[1]

(1) Mizushima, this journal, 1 (1926), 83 & 115.

The values of ε at higher temperatures are independent of wave length and equal to those for static field even for the wave length of 3.08 metres. As the temperature is gradually lowered, the absorption of wave becomes stronger and ε undergoes a great change at a certain wave length. For instance at $-20°$, ε of amyl alcohol for the wave length of 50 metres is 19, a value not far from the static dielectric constant, then ε decreases to 4, a value approaching to the square of the refractive index for the visible light (N_ν^2). At still lower temperatures e.g. at $-60°$ where the absorption of wave again decreases, all the values of ε for different wave lengths approach to one another and are not far from N_ν^2. This was not observed for ethyl alcohol, but if the experiment could be carried out at sufficiently low temperatures, liquid ethyl alcohol would also show this end of anomalous dispersion.

In short the dielectric constants of alcohols and glycerine change continuously from the large value for the static field to the small value nearly equal to N_ν^2 and the region of anomalous dispersion accompanying intense absorption shifts to longer wave lengths as the temperature is lowered.

Here we have a relation between the anomalous dispersion and absorption of electromagnetic waves, which is quite analogous to that for the visible light. But it should be noticed that an absorption band in the visible as well as in the infra-red or ultra-violet parts is not so much effected by the temperature variation, while a band in the electric spectrum undergoes an enormous effect and the band shifts to the longer wave lengths as the temperature is lowered. From the measurement of the anomalous electric absorption by Drude,[1] the wave length of 70 cm. is often adopted, without the indication of temperature, as the characteristic wave length of alcohols, but when the absorption band in the electric spectrum is considered, the indication of temperature must not be forgotten as is shown above.[2]

As to the anomalous absorption for a definite wave length, Drude noticed in his paper that the absorption by alcohols becomes stronger as the temperature is lowered. However, such is the case only at comparatively higher temperatures. As the temperature is lowered, the absorption reaches a maximum, then decreases till it almost disappears. It is evident that all of the Drude's experiments were carried out at the temperatures higher than that for this maximum absorption.

Now the above results can be discussed from the view-point of Debye's dipole theory, of which a short explanation was already given in Part IV.[3]

(1) Drude, *Z. physik. Chem.*, **23** (1897), 267.
(2) Landolt-Börnstein's "Tabellen," (1923), p. 807.
(3) Mizushima, this journal **1** (1926), 143.
Debye, *Verh. Deut. Physik. Ges.* **15** (1913), 770.

The distribution function of dipole axes for the angle θ under the periodic force $Ke^{i\omega t}$ is

$$F=A\left(1+\frac{1}{1+\frac{i\omega\rho}{kT}}\ \frac{m}{kT}\ Ke^{i\omega t}\cos\theta\right)\cdots\cdots\cdots\cdots\cdots(1)$$

where

$$\rho=8\pi\eta a^3$$

and A is a constant, η the viscosity, a the radius of the molecule, m the moment of dipole, k Boltzmann's constant and T the absolute temperature.

This becomes for a static field :

$$F_0=A\left(1+\frac{m}{kT}K\cos\theta\right)\cdots\cdots\cdots\cdots\cdots\cdots\cdots(2)$$

The difference in the distribution between a static and an alternating field is, therefore, determined by the expression $\left(1+\frac{i\omega\rho}{kT}\right)$, in which

$$\frac{\rho}{kT}=\frac{8\pi\eta a^3}{kT}=\tau\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(3)$$

expresses the time of relaxation of the molecule. So long as the period of external field is very great as compared with τ, the distribution of the dipole axes will remain practically constant. Consequently the dielectric polarization is independent of wave length and equal to that for the static field. If, however, the external period approaches to the time of relaxation, F becomes different from F_0 and the medium will show anomalous dispersion. We see in equation (3) that the value of τ is proportional to the viscosity η and the cube of the molecular radius a^3 and inversely proportional to the absolute temperature T. Therefore the anomalous region will shift to the longer wave lengths as the temperature is lowered and the viscosity becomes greater. The effect will be the same as we proceed from lower to higher alcohols, because the molecular radius as well as the viscosity becomes greater. These are all what are confirmed by the above experiments.

From equation (1) we can calculate the dielectric constant ε for an alternating field of the frequency $\frac{\omega}{2\pi}$,

$$\varepsilon=\left\{\frac{\left(\frac{\varepsilon_0}{\varepsilon_0+2}\right)^2+\frac{\omega^2\rho^2}{k^2T^2}\left(\frac{\varepsilon_\infty}{\varepsilon_\infty+2}\right)^2}{\left(\frac{1}{\varepsilon_0+2}\right)^2+\frac{\omega^2\rho^2}{k^2T^2}\left(\frac{1}{\varepsilon_\infty+2}\right)^2}\right\}^{\frac{1}{2}}\cos^2\frac{\varphi}{2}$$

where

$$\tan\varphi=\frac{\omega\rho}{kT}\,\frac{\varepsilon_0+2}{\varepsilon_\infty+2}\,\frac{1-\dfrac{\varepsilon_\infty}{\varepsilon_0}}{1+\dfrac{\omega^2\rho^2}{k^2T^2}\left(\dfrac{\varepsilon_0+2}{\varepsilon_\infty+2}\right)^2\dfrac{\varepsilon_\infty}{\varepsilon_0}}$$

The values of $\varepsilon_{calc.}$ are calculated for the wave length of 3.08 metres and 50 metres according to the method as explained in Part IV[1] and are compared with the observed values ($\varepsilon_{obs.}$). As shown in the above tables, $\varepsilon_{calc.}$ agrees pretty well with $\varepsilon_{obs.}$

For glycerine we have no data for a. Therefore no systematic discussion can be made. If, however, we take at 18° the value of ε_0 equal to 43 (Graffunder[2]), that of η to 10.69 (Jones[3]), that of ε_∞ to 2 and that of $\varepsilon_{obs.}$ to 25.5 (present experiment), then we obtain the following value of a for glycerine:

$$a=2.8\times10^{-9}\text{ cm.}$$

This is not a reasonable value, because the molecular radius is of the order of 10^{-8} cm. even for simple diatomic molecules and that for a complex molecule such as glycerine must be greater than this. We must, therefore, agree with Bock[4] that Debye's formula does not hold for glycerine. As the viscosity of glycerine is abnormally great, it is very doubtful whether η in the resistance term $8\pi\eta a^3$ is equivalent to the mass viscosity of glycerine. If glycerine be a colloidal system and its mass viscosity must be considered as the viscosity of heterogeneous mixture,[5] the effective viscosity acting on the rotation of a molecule will be quite different from ordinary viscosity. Then we can naturally consider the glycerine to be an exception for Debye's theory.

Allowing this exception, the result of the author's experiment may be considered to be the first experimental evidence of the dipole theory on the anomalous dispersion of electric waves.

The author wishes to express his best thanks to Prof. M. Katayama for his kind guidance.

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(1) Loc. cit.
(2) Graffunder, *Ann. Physik.* 70 (1923), 225.
(3) Jones, *Phil Mag.*, (5) 37 (1894), 451.
(4) Bock, *Z. Physik*, 31 (1925), 534.
(5) Einstein, *Ann. Physik*, 19 (1905), 289.

THERMODYNAMIC STUDIES ON ZINC IODIDE AND MERCUROUS IODIDE.[1]

By Fusao ISHIKAWA and Eiichi SHIBATA.

Received June 29, 1926. Published August 28, 1926.

I. The Fictitious Heat of Solution of Zinc Iodide. As is well known, the fictitious heat of solution of an anhydrous salt can be determined by the following thermodynamic relations, existing between the temperature coefficients of the electromotive forces, $\left(\frac{dE}{dT}\right)_A$ and $\left(\frac{dE}{dT}\right)_B$, of the reversible cells with and without solid salt.[2]

$$(Q)_T = T\left[\left(\frac{dE}{dT}\right)_A - \left(\frac{dE}{dT}\right)_B\right] n \cdot 23074 \cdots\cdots (1)$$

$$(Q)_T = T\left(\frac{dE}{dC}\right)_T \left(\frac{dC}{dT}\right) n \cdot 23074 \cdots\cdots\cdots\cdots (2)$$

The authors have determined the fictitious heat of solution of zinc iodide with the aide of formula 1. In the case of zinc iodide, formula 2 is not suitable for this purpose, owing to the experimental difficulties in determining the temperature coefficient of solubility of zinc iodide as it has been known to be exceedingly small.

The following cells were constructed and their electromotive forces were measured at several temperatures, the results are shown in tables 1 and 2.

Zn amalgam 10%	Zinc iodide, saturated solution, Hg_2I_2 solid salt	Hg……Cell A.
Zn amalgam 10%	Zinc iodide, saturated solution, Hg_2I_2	Hg……Cell B.

(1) This is the abstract of a paper which will be published in *The Science Reports of the Tôhoku Imperial University.*

(2) E. Cohen, and others, *Z. Physik. Chem.* **93**, (1918), 43; **94**, (1920), 210; **105**, (1923), 155.

TABLE 1.

Cell A, with solid salt.

Temperature degree	Electromotive forces		
	Observed (mean) volt	Calculated volt	Calc.—obs.
20.00	0.52358	0.52358	0.00000
22.50	0.52391	0.52395	+0.00004
25.00	0.52429	0.52429	0.00000
27.50	0.52461	0.52462	+0.00001
30.00	0.52489	0.52492	+0.00003
32.50	0.52519	0.52521	+0.00002
35.00	0.52551	0.52548	−0.00003

TABLE 2.

Cell B, without solid salt.

Temperature degree	Electromotive forces		
	Observed (mean) volt	Calculated volt	Calc.—obs.
20.00	0.52278	0.52300	+0.00022
22.50	0.52350	0.52356	+0.00006
25.00	0.52415	0.52415	0.00000
27.50	0.52478	0.52477	−0.00001
30.00	0.52543	0.52543	0.00000
32.50	0.52612	0.52612	0.00000
35.00	0.52685	0.52685	0.00000

By the method of least square the following equation was obtained for the cell A and the electromotive forces calculated are given in the third column of Table 1.

$$E=0.52420+0.0001336\ (t-25)-0.000001496\ (t-25)^2$$

which gives

$$\left(\frac{dE}{dT}\right)_{A,\,298}=0.0001336 \quad \text{volt/degree.}$$

The electromotive forces of the cell B can be expressed by the equation:

$$E=0.52415+0.0002427(t-25)+0.0000027(t-25)^2$$

and the calculated values are given in the third column of Table 2. From the above equation we obtain,

$$\left(\frac{dE}{dT}\right)_{B,298} = 0.0002427 \text{ volt/degree.}$$

Substituting these numerical values for $\left(\frac{dE}{dT}\right)_A$ and $\left(\frac{dE}{dT}\right)_B$ in the formula 1, we can calculate the fictitious heat of solution of zinc iodide, thus

$$(Q)_{298} = 298.1(0.0001336 - 0.0002427)46148 = -1500 \text{ cal./mol.}$$

II. The Heat of Formation of Zinc Iodide. The heat of formation of zinc iodide can be determined by applying Gibbs-Helmholtz's equation to the Cell A, in combination with the heat of formation of mercurous iodide. If the figure 14200 cal. (Nernst,[1] Bernoulli[2]) be taken as the heat of formation of mercurous iodide (HgI), the heat of formation of zinc iodide will be:

$$2Hg + I_2 = Hg_2I_2 \; ; \; \Delta H_{298} = -28400 \text{ cal.}$$
$$Zn + Hg_2I_2 = ZnI_2 + 2Hg \; ; \; \Delta H_{298} = -22360 \text{ cal.}$$

The heat change in drawing an atom of zinc out of the amalgam being null, hence

$$Zn + I_2 = ZnI_2 \; ; \; \Delta H_{298} = -50760 \text{ cal.}$$

This value is found to be a little larger than that obtained by T. J. Webb[3] as the result of his study on the cell: Ag | AgI, ZnI_2 | Zn amalgam.

III. The Free Energy of Formation and the Entropy of Mercurous Iodide. E. Cohen and his co-workers[4] expressed the electromotive force of the cell: Cd amalgam | CdI_2, Hg_2I_2 | Hg as follows

$$E_1 = 0.41886 + 0.0003642\,(t-30) - 0.0000003\,(t-30)^2.$$

Hence

$$\left(\frac{dE_1}{dT}\right)_{298} = 0.0003672 \text{ volt/degree.}$$

The temperature coefficient of the cell: Cd | solution | Cd amalgam has been given by the expression[5]

$$\left(\frac{dE_2}{dT}\right)_{298} = -0.000244 \text{ volt/degree.}$$

Then the entropy change ΔS_{298} corresponding to the reaction: $Hg_2I_2 + Cd = CdI_2 + 2Hg$ may be calculated thus:

$$\Delta S_{298} = 2F\left\{\left(\frac{dE_1}{dT}\right)_{298} + \left(\frac{dE_2}{dT}\right)_{298}\right\} = 5.68 \text{ entropy units.}$$

from which the entropy of mercurous iodide may be evaluated, as the entro-

(1) Nernst. *Z. physik. Chem.*, **2** (1888), 23.
(2) Bernoulli, *Helvetica Chim. Acta*, **2** (1919), 720.
(3) Webb, *J. Phys. Chem.*, **27** (1923), 448.
(4) *Z. physik. Chem.*, **94** (1920), 210.
(5) Gerke, *Chem. Rev.*, **1** (1925), 377.

pies[1] of Hg, Cd and CdI_2 are known to be $S_{Hg}=17.8$, $S_{Cd}=11.8$ and $S_{CdI_2}=38.7$,

$$S_{Hg_2I_2}=56.8 \text{ entropy units.},$$

which is quite consistent with the value $S_{Hg_2I_2}=56.76$, calculated with the aid of the formula proposed by Latimer[2] for the entropy of solid salt:

$$S_{298}=\tfrac{3}{2}\cdot R \ln A-0.94 \ (A \text{ being atomic weight}).$$

The entropy change and the free energy change in the formation of mercurous iodide will be:

$$2Hg+I_2=Hg_2I_2\ ;\ \Delta S_{298}=-5.4 \text{ entropy units},$$

$$(S_{I_2}=2\times 13.3)$$

$$2Hg+I_2=Hg_2I_2\ ;\ \Delta F_{298}=\Delta H_{298}-T\Delta S_{298}=-26790 \text{ cal.}$$

IV. The Free Energy of Formation of Zinc Iodide. This can be calculated as follows:

$$Zn+Hg_2I_2=ZnI_2+2Hg\ ;\ \Delta F_{298}=-2EF=-24195 \text{ cal.}$$

$$2Hg+I_2=Hg_2I_2\ ;\ \Delta F_{298}=-26790 \text{ cal.}$$

Hence

$$Zn+I_2=ZnI_2\ ;\ \Delta F_{298}=-50985 \text{ cal.}$$

This result may be compared with that obtained by the entirely different process. The electromotive force of the cell involving the reaction $Zn+2AgI=ZnI_2+2Ag$, has been given by T. J. Webb[3]: $E=0.3987$.

Hence

$$Zn+2AgI=ZnI_2+2Ag\ ;\ \Delta F_{298}=-2EF=-18400 \text{ cal.}$$

and

$$Ag+\tfrac{1}{2}I_2=AgI\ ;\ \Delta S_{298}=3.4 \text{ entropy units.}^{(4)}$$

$$Ag+\tfrac{1}{2}I_2=AgI\ ;\ \Delta H_{298}=-15100 \text{ cal.}^{(3)}$$

$$Ag+\tfrac{1}{2}I_2=AgI\ ;\ \Delta F_{298}=\Delta H-T\Delta S=-16114 \text{ cal.}$$

so that

$$Zn+I_2=ZnI_2\ ;\ \Delta F_{298}=-50628 \text{ cal.}$$

The agreement is fairly satifactory.

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(1) Lewis-Randall, "Thermodynamics," 1923; Webb, *J. phys. Chem.*, **29** (1925), 816.
(2) *J. Am. Chem. Soc.*, **43** (1921), 818.
(3) *J. Phys. Chem.*, **27** (1923), 448.
(4) Lewis-Randall, loc. cit.

ON THE EFFECTS OF GASES UPON THE SURFACE TENSIONS OF SOME LIQUIDS.[1]

By Bun-ichi TAMAMUSHI.

Received June 29, 1926. Published August 28, 1926.

Introduction. Surface tension, being a property of the boundary surface of phases, should be effected by the nature of phases on both sides of the surface. According to the classical works of Quincke,[2] Kundt,[3] and Guye and Renard,[4] it is evident that air has a certain effect, though not so considerable, upon the surface tension of pure water. In later years Ferguson[5] studied the effects of air and carbon dioxide on the surface tensions of some organic liquids. The present paper contains the results of measurements made on the following pairs of gases and liquids. Gas : air, carbon dioxide, nitrous oxide, hydrogen sulphide. Liquid : water, ethyl alcohol, ethyl ether, carbon bisulphide, carbon tetrachloride.

Experimentals. The apparatus of Ramsay and Shields[6] is somewhat modified in the present research as is shown in Fig. 1, particularly for the purpose of easily saturating solvent with gas. This is done by the side tube B, which is connected to a generator of gas and also to a manometer. The top of the wide tube A is provided with a good stop cock and the whole U tube is protected, to its neck, by a water jacket of temperature constant within the fluctuation of less than $\pm 0.1°$.

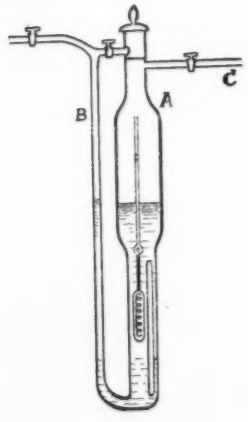

Fig. 1.

Two capillary tubes were very carefully selected and examined and their radii have been found to be 0.0142 cm. and 0.0166 cm. respectively. The rise of liquid in the capillary tube was measured by a cathetometer of Société Genevoise with an accuracy to 0.005 cm., and corrections due to the curvature of meniscus were calculated by means of Lord Rayleigh's[7] formulae.

(1) Read before the Chemical Society of Japan, October 1924.
(2) *Pogg. Ann.*, **160** (1877), 573.
(3) *Wied. Ann.*, **12** (1881), 538.
(4) *J. chim. phys.*, **5** (1907), 81.
(5) *Phil. Mag.*, (6), **28** (1914), 403.
(6) *J. Chem. Soc.*, **63** (1893), 1089.
(7) *Proc. Roy. Soc.*, [A] **92** (1915), 184.

In the course of measurement the capillary rise of a pure solvent is at first read under its own vapour pressure (the apparatus being previously evacuated through another side tube C) and then letting the gas pass into the solvent under a certain pressure less than one atmosphere and when the equilibrium is attained the height of the capillary column is again measured, due care being taken of the constancy of temperature in the jacket during all these processes.

The surface tension is calculated by the following formula:

$$\sigma = \frac{1}{2} g\, r\, (h+h')\, (D-d)$$

where g: gravity constant, r: radius of capillary tube, h: capillary rise read by cathetometer, h': correction term, D: density of liquid determined by pyknometer in each case, d: density of gas phase, which was taken from Landolt-Börnstein's Tables and the related small corrections have been calculated by the law of ideal solution. The depression of surface tension is expressed in percentage as $100\frac{\Delta\sigma}{\sigma}$, $\Delta\sigma$ being the difference of surface tensions between solvent and solution, σ being the surface tension of pure solvent. The experimental results are shown in the following tables, in which p denotes the pure solvent and s solution.

TABLE 1. Air.

Solvent	Temp.	$100\frac{\Delta\sigma}{\sigma}$
Water	20	0.22
Ethyl alcohol	19	0.46
Benzene	18	0.32
Ethyl ether	20	0.40

TABLE 2. Carbon dioxide.

Solvent	Temp.		$h+h'$	$D-d$	σ	$100\frac{\Delta\sigma}{\sigma}$
Water	18.0	p	8.694	0.9986	70.95	0.83
		s	8.631	0.9974	70.36	
CCl_4	25.0	p	1.9633	1.5822	25.27	0.96
		s	1.9453	1.5815	25.03	
CS_2	24.8	p	2.960	1.2620	30.39	0.95
		s	2.935	1.2607	30.10	
$(C_2H_5)_2O$	25.3	p	2.759	0.7067	15.82	0.97
		s	2.721	0.7078	15.67	
C_2H_5OH	25.3	p	3.317	0.7860	21.21	0.99
		s	3.287	0.7854	21.00	
C_6H_6	25.1	p	3.803	0.8714	26.96	0.96
		s	3.771	0.8705	26.70	

TABLE 3. Nitrous oxide.

Solvent	Temp.		$h+h'$	$D-d$	σ	$100\frac{\Delta\sigma}{\sigma}$
Water	25.2	p	8.685	0.9968	70.43	0.75
		s	8.635	0.9951	69.90	
C_2H_5OH	25.1	p	3.319	0.7870	21.25	0.97
		s	3.292	0.7858	21.04	
$(C_2H_5)_2O$	25.0	p	2.774	0.7067	15.95	0.82
		s	2.750	0.7071	15.82	
CCl_4	24.8	p	1.962	1.5822	25.26	0.96
		s	1.943	1.5823	25.01	

TABLE 4. Hydrogen sulphide.

Solvent	Temp.		$h+h'$	$D-d$	σ	$100\frac{\Delta\sigma}{\sigma}$
Water	15.2	p	8.740	0.9990	71.36	1.19
		s	8.640	0.9985	70.51	
C_2H_5OH	16.1	p	3.388	0.7948	22.15	1.26
		s	3.340	0.7960	21.87	
C_6H_6	15.3	p	3.954	0.8829	28.67	1.22
		s	3.900	0.8843	28.32	

TABLE 5.

Solvent	Gas	Concentration C	$C^{\frac{1}{3}}$	$100\frac{\Delta\sigma}{\sigma}$
Water	Air	0.00236	0.133	0.22
	N_2O	0.104	0.470	0.75
	CO_2	0.145	0.525	0.83
	H_2S	0.334	0.694	1.19
C_2H_5OH	Air	0.0232	0.285	0.46
	N_2O	0.647	0.865	0.97
	CO_2	0.693	0.885	0.99
	H_2S	1.870	1.232	1.26
C_6H_6	Air	0.0205	0.274	0.32
	CO_2	0.571	0.830	0.96
	H_2S	1.084	1.027	1.22

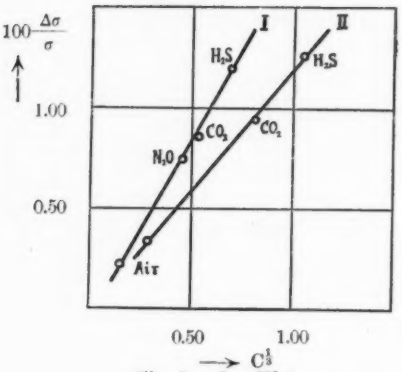

Fig. 2. I: Water.
II: Benzene.

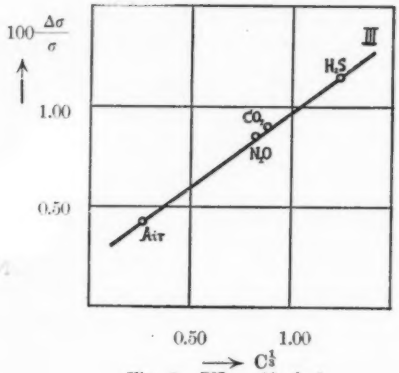

Fig. 3. III: Alcohol.

Discussions. The depressive effects of air upon these liquids are in the mean not greater than five percent; values of the same order were obtained also by the other authors already mentioned.

If we compare the values of $\frac{\Delta\sigma}{\sigma}$ with each other for a given gas and different liquids, it is remarkable that they are almost constant in each series, that is, the greater the surface tension the greater the effect of depression. It must be mentioned that similar facts were observed by Ferguson in his experiments above refered. The rule of this kind is certainly not insignificant, however its theoretical explanation may not be simple as the complex nature of adsorption and of other related phenomena must be taken in consideration.

Table 5 shows the relation between the values of $\frac{\Delta\sigma}{\sigma}$ and the concentrations of different gases dissolved in the same solvent. The values of solubilities are quoted from Seidell's Tables except one, i.e. the solubility of hydrogen sulphide in bengene, which has been determined by the author, the details of the method being here omitted. As it is shown in this table or in Fig. 2 and 3, the relation between the cube root of concentration and $\frac{\Delta\sigma}{\sigma}$ is nearly linear in each case, that is, for a system of same liquid and different gases we have an empirical relation as follows:

$$\frac{\Delta\sigma}{\sigma} = kC^{\frac{1}{3}} + a$$

where k and a are certain constants. In other words, as a is in general very small, $\frac{\Delta\sigma}{\sigma}$ is almost proportional to the linear distances of molecules of the adsorbate. It may be also remarked that this formula has in its form a certain analogy with the adsorption isotherm of Freundlich.

The author wishes to express his sincere thanks to Prof. M. Katayama for his kind guidance during this work.

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ON THE CATALYTIC ACTION OF JAPANESE ACID EARTH. II. THE ACTION ON OXIMES.

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Mailhe and Godon[1] have noticed that aldoximes and ketoximes were transformed into nitriles by the catalytic action of alumina at high temperature. The action of Japanese acid earth on oximes, therefore, was studied by the present writer from the view point of contact action, and the following interesting results were obtained.

1. Acetophenone oxime. 20 grams of acetophenone oxime (m.p. 58–59°) mixed with 10 grams of Japanese acid earth in a flask, were heated gradually on an oil-bath. When the temperature of the bath reached 180°, a violent reaction suddenly took place as we sometimes meet in case of Beckmann's rearrangement of oximes, and whereas some volatile liquid distilled out through the side tube of the flask, a solid reaction product remained in it. Both the liquid and solid reaction products were treated separately with ether and then hot water; the ethereal solution was treated with ammonia and dilute hydrochloric acid successively to get off the acidic and basic substances from a neutral substance which is formed simultaneously by the reaction. Acetic and benzoic acids from the acidic fraction, and ammonia and aniline from the basic one were isolated and confirmed to be so by their chemical properties. Benzonitrile was isolated from the neutral reaction product, which was confirmed, by saponification with alcoholic potash, by transforming into benzoic acid (m.p. 121°) and ammonia. Acetophenone was also noticed to occur with the nitrile in the neutral reaction product in isolating in a pure state. From the hot aqueous solution, acetanilide (m.p. 115°, N=10.32%) was obtained in a pure state. The yield of the reaction products is shown in Table 1.

2. Benzophenone oxime. When benzophenone oxime (m.p. 139°) was treated in the same manner as the acetophenone oxime, the rearrangement

(1) Mailhe and Godon, *Bull. Soc. Chim.*, (4), **23** (1918), 18.

was noticed to take place at 145° and benzanilide (m.p. 160°), benzonitrile, benzoic acid and other substances of unknown chemical nature were actually obtained from the reaction product, and the quantity of these substances is shown in Table 1.

3. **Menthone oxime.** Menthone oxime (m.p. 53–55°), when treated with the catalyst at 200°, was transformed into decylenic acid, methonitrile, menthone and a hydrocarbon, and the yield of these substances is shown in Table 1.

TABLE 1.

Oximes	Sample used gr.	Acid gr.	Base gr.	Acid amide gr.	Nitrile gr.	Neutral subst. gr.	NH_3
Acetophenone oxime	20.0	0.69	0.81	1.33	0.55	4.20	+
Benzophenone oxime	12.5	0.12	0.63	2.04	0.04	4.81	+
Menthone oxime	12.9	0.46	0.60	—	0.55	5.81	+

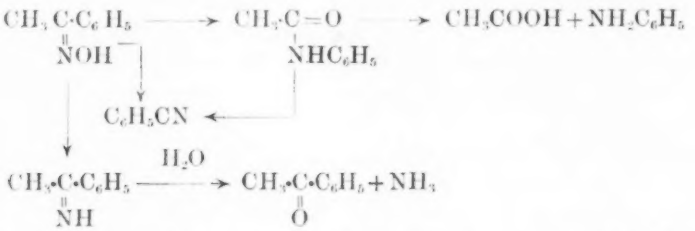
As a matter of fact, acids, nitriles, acid amides and bases were formed from oximes by contact action of Japanese acid earth, and the nitriles were naturally regarded as forming directly from the oximes as in the case of the catalytic action of alumina and also indirectly from acid amides or isoximes which resulted from the oximes by the Beckmann rearrangement. In the present case, the writer was inclined to believe that the Beckmann rearrangement was one of the principal reactions of oximes caused by the contact action of Japanese acid earth at about 150–200°, since acetanilide and benzanilide were actually isolated with a large yield from the reaction products of acetophenone and benzophenone oximes respectively, and aniline which occurs in the reaction product in both cases, was explained to be formed by hydrolysis of the anilides. In order to confirm the above assumption for the transformation of anilides into aniline, acid and nitrile, by the contact action of the earth, 10 grams of acetanilide and of benzanilide were passed respectively on the catalyst heated at 300°, aniline, acids and nitrile were confirmed to occur in the reaction products as will be seen in the following table.

TABLE 2.

Acid amides	Acid amide unchanged gr.	Nitrile	Base (aniline) gr.	Acid gr.	NH_3
Acetanilide	0.55	a little	1.87	0.014	+
Benzanilide	0.55	a little	0.37	0.012	+

When, however, 20 grams of benzonitrile (b. p. 183—184°; density = 1,0068) were passed on the same catalyst heated at 250°, no appreciable reaction was noticed to take place.

Thus, the transformation of ketoximes by the contact action of Japanese acid earth, into their isomeric acid amides, nitriles, acids, amines and ketones was represented with an example of acetophenone oxime, by the following scheme:



The formation of acetophenone from its oxime was explained by the direct hydrolysis of the oxime on the one side, and on the other by assuming the formation of methyl phenyl-ketimine as an intermediate, as indicated by Lachman.[1]

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STUDIES ON MERCAPTALS OF SUGARS. I. NORMAL BUTYL MERCAPTALS OF SUGARS.[2]

By **Yoshisuke UYEDA** and **Jinzō KAMON.**

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Fisher[3] found that a glucoside was produced by the condensation of the sugar and the alcohol in presence of hydrochloric acid. When the aldehyde being treated with the mercaptan, a substance "mercaptal," named by Baumann,[4] was prepared. Fisher[5] obtained various mercaptals in crystalline

(1) Lachman, *J. Am. Chem. Soc.*, **46** (1924), 1477.

(2) Read before the Chemical Society of Japan, April 6, 1924. The original paper will be published in the *Journal of the Chemical Society of Japan*, and this is an abstract from the original one.

(3) Fisher, *Ber.*, **26** (1893), 2400.

(4) Baumann, *Ber.*, **18** (1885), 884.

(5) Fisher, *Ber.*, **27** (1894), 673.

form by the condensation of sugars and mercaptans in presence of concentrated hydrochloric acid. He used ethyl and amyl mercaptan.

The present authors have studied on the normal butyl mercaptals of various sugars and obtained various crystalline mercaptals. Five monoses, arabinose, glucose, galactose, mannose and rhamnose; three dioses, lactose, maltose and sucrose were tried and the mercaptals thus prepared were crystallized from dilute alcohol. Xylose and fructose were tried, but ended in negative results.

The new mercaptals of sugars prepared by us have the following formula, which were ascertained by the analysis.

Glucose-N-butyl mercaptal		$C_6H_{12}O_5(C_4H_9S)_2$
Galactose	,,	$C_6H_{12}O_5(C_4H_9S)_2$
Mannose	,,	$C_6H_{12}O_5(C_4H_9S)_2$
Rhamnose	,,	$CH_3C_5H_9O_4(C_4H_9S)_2$
Arabinose	,,	$C_5H_{10}O_4(C_4H_9S)_2$
Maltose	,,	$C_{12}H_{22}O_9(C_4H_9S)_4$
Lactose	,,	$C_{12}H_{22}O_9(C_4H_9S)_4$
Sucrose	,,	$C_{12}H_{22}O_9(C_4H_9S)_4$

The physical constants of these mercaptals have been measured and are tabulated as follows.

		M.p.	Sp. rotation.
Glucose-N-butyl mercaptal		124°	$[\alpha]_D^{12°} = +27.00$
Galactose	,,	123	,, $= +12.67$
Mannose	,,	117	$[\alpha]_D^{8°} = +16.45$
Rhamnose	,,	119	,, $= +16.49$
Arabinose	,,	111.5	,, $= +14.00$
Maltose	,,	126	,, $= +12.00$
Lactose	,,	106	,, $= +23.55$
Sucrose	,,	123	,, $= +3.71$

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STUDIES ON MERCAPTALS OF SUGARS. II. NORMAL PROPYL MERCAPTALS OF SUGARS.

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Normal butyl mercaptals of sugars have been studied by one of the authors (Uyeda) and Kamon, and are described in the previous paper. Now, the authors have tried to study on the normal propyl mercaptals of sugars, according to Fisher's method. The outline of the results is reported in this paper.

Experimental. Mercaptals are prepared by the following method: Each sugar is dissolved in equal quantity of concentrated hydrochloric acid (sp. gr. 1.20), to whose solution, a little excess of molecular proportion of normal propyl mercaptan being added, well shaken and stand over night. Most of them begin to crystallize out within an hour. The crystalline product is filtered, washed with water, and dried on the porous tile. The crude products thus obtained are purified by the recrystallization from dilute alcohol, the mercaptals are nice white crystalline needles.

The physical constants and the results of analysis are summarized in the following tables:

TABLE 1. Properties of Mercaptals.

	M.p.	Sp. rotation $[\alpha]_D^{17°}$
Glucose N-propyl mercaptal	147°	+41°
Galactose ,,	129	+27.5
Mannose ,,	125	+31
Rhamnose ,,	130	+10
Arabinose ,,	128	+29
Maltose ,,	146	+25
Sucrose ,,	146	+13.5

TABLE 2. Analysis of Mercaptals.

		Sulphur	
		Calc. %	Found %
Glucose N-propyl mercaptal	$C_6H_{12}O_5(C_3H_7S)_2$	20.38	20.07
Galactose ,,	$C_6H_{12}O_5(C_3H_7S)_2$	20.38	20.15
Mannose ,,	$C_6H_{12}O_5(C_3H_7S)_2$	20.38	20.01
Rhamnose ,,	$CH_3C_5H_9O_4(C_3H_7S)_2$	21.47	21.24
Arabinose ,,	$C_5H_{10}O_4(C_3H_7S)_2$	22.53	22.20
Maltose ,,	$C_{12}H_{22}O_9(C_3H_7S)_4$	20.98	20.61
Sucrose ,,	$C_{12}H_{22}O_5(C_3H_7S)_4$	20.98	20.68

The sulphur was determined by using sodium peroxide in Parr bomb.

Other sugars than these, namely xylose, fructose and lactose, were tried, but ended in negative results.

Summary.

The following sugars were obtained as new crystalline mercaptals by treatments with normal propyl mercaptan :—

Three hexoses, glucose, galactose and mannose ; one pentose, arabinose, one methyl pentose, rhamnose ; two dioses, maltose and sucrose.

Our sincere thanks are due to Assistant Professor Ishinada, who kindly checked carefuly the physical constants of our samples.

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